EXTRACTION RATES AND POROSITY CHANGES OF COALS IN SUPERCRITICAL THF

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Important facets of the thermal processing of coals in a dis-solving medium, such as that which occurs in liquefaction or extrac-tion, are the rate of dissolution and the concomitant change in the surface structure of the coal. The interaction between these two related parameters is being studied by extracting coals in a flow-through cell under supercritical conditions and measuring the rates of extraction by on-line ultraviolet spectroscopy and the changes in pore structure of the coal by in situ small-angle X-ray scattering. The advantages of utilizing supercritical fluids in this project are the solvent densities, which are similar to liquids, the high solu-bility parameters, and yet low viscosities, similar to gases. For these experiments the solvent should be composed of first row ele-ments and not have significant absorption in the uv. In addition, alcohols cannot be used since they destroy the aluminum windows of the extraction cell. Several solvents were tested in these investi-gations, and supercritical tetrahydrofuran (THF) was the only one found satisfactory for both measurements. The supercritical THF gave good yields of extract from even lignites, and the extracted material remained soluble in liquid THF.

EXPERIMENTAL

The solvent in these studies was uninhibited HPLC grade THF (Fisher), used as received. Coal was dried in an inert atmosphere or in a vacuum prior to the extraction. Ultimate analysis (maf) for the Wyodak subbituminous coal (Clovis Point) was H, 5.2; C, 70.9; N, 0.92; S, 0.60; O (ind.), 22.3. Proximate analysis (mf) was volatile matter, 44.2; ash, 8.4; fixed carbon (ind.), 47.5.

Two different extraction cells have been used for the two types of measurements. The apparatus in which the extraction kinetics were measured by uv absorption consisted of an Isco LC-5000 syringe pump connected to a 5 cm x 4.6 mm (LC precolumn) extraction cell. The cell and steel inlet tubing were heated in a Varian 1400 aerograph GC. The cell capacity was 0.2 g. Effluent from the cell was carried fr. the oven via a 1/16-inch steel tubing to a 1 m x 0.32 mm fused silica capillary (no phase coating), which served as the cell for the uv detector. The polyimide outer coating was removed from a portion of the capillary which was in the beam path of a Kratos 700 LC detector (254 nm). After passing through the uv detector, the capil-lary was connected to a Whitney SS-21RS2 restrictor valve to maintain the pressure in the system. The eluent was collected, and the weight of extract was determined after evaporation of the solvent.

Analog signals from the uv detector were digitized with an Omega WB-31 12-bit A/D converter and transferred to a Tandy 2000HD computer via RS-232C. Data was collected and stored to disk at 2 points/s. The area under the uv response curve was divided into 100 equal time segments and the proportional area determined for each segment. The

proportional areas were multiplied by the extract weight, giving the weight of extract per unit time. This normalization assumes that the response across the curve remains constant, which was determined to be true for extraction of 3 g of coal in a large cell where individual fractions were collected and weighed.

The extraction cell for the small-angle scattering studies consisted of two electrically heated flanges which hold the aluminum/berylium windows and a stainless steel block which gives a sample depth of 0.07 inches between the two windows. Molybdenum K_α radiation was used in these studies. Details of the collimation system and position sensitive detector are available elsewhere (1). Analysis of the scattering data was based on a model developed by Kalliat, Kwak, and Schmidt (2). Pore structure parameters calculated for thermally treated lignites have been shown to be in close agreement with independent measurements (3).

RESULTS AND DISCUSSION

A series of kinetic experiments were carried out with Wyodak subbituminous coal (Clovis Point) in the flow-through cell with on-line uv detection. In each of these runs, a dewaxing preextraction stage at a temperature of $120^\circ C$ was utilized to remove an initial surge of material, whose elution was monitored until no detector response was observed. The material extracted at this low temperature (2% mf basis) was mainly aliphatic (fatty acids), similar to the Montan wax, which is normally extracted with noncritical solvents and is not believed to be covalently bonded or "matrix trapped" material.

The X-ray scattering pattern of the Wyodak coal after extraction at $120^\circ C$ and 4.5 MPa indicated that the dewaxing had an effect on the pore structure, causing a modest increase in the micropore parameters (Table 1). The micropore specific surface increased from 58 m^2/g to about 290 m^2/g. The corresponding increase in micropore volume was 0.019 cm^3/g, which would suggest about a 2% loss of mass if the new pore structure is formed in the wake of the dissolved component.

The supercritical extractions were carried out by rapidly increasing the temperature of the system ($30^\circ C$/min) in the GC oven to the desired extraction temperature where the temperature was held constant (isothermal stage). UV response data for the Wyodak coal were recorded for four extraction temperatures from 325 to $400^\circ C$ at 15.2 MPa and flow rates of 1 ml/min. Run times were about one hour. Two extractions were conducted at $380^\circ C$ at lower pressures (5.5 and 10.3 MPa) for comparison with the 15.2 MPa run. The solvent containing the extracted material was collected after the restrictor valve. The solvent was removed and the extract weighed. The yield data from the four experiments at 15.2 MPa and two experiments conducted at lower pressures are shown in Table 2. The yields at the high temperatures (350° and above) at 15.2 MPa were essentially the same and were approximately three times the yield obtained at either low temperature (325°) or low pressures. We distinguish then, three classes of extracted coal material, the preextraction wax, the low-temperature extract (easily extracted material), and the high-temperature extract (less easily extracted material). The composition of the low- and high-temperature extracts was similar, consisting of high molecular weight aliphatic and aromatic material. The higher yields at the higher pressure may be due to the higher solvating power of the supercritical fluid at higher densities, which are obtained at

higher pressure, or may be due to a physical effect such as solvent being forced into a micropore.

The uv response curve for the 380°C extraction of Wyodak is shown in Figure 1. The curve does not include the preextraction step, instead it begins with the rapid temperature increase. From the uv response curve, the amount of coal material being extracted at each instant and the amount accumulated at each time interval (x) was determined. The natural log of the difference between the total amount of extract (a) and the accumulated amount at each interval (x) was plotted versus time. The first half of the curve was linear, indicating first-order kinetics. The slope of this part of the curve was used to determine an apparent rate constant. Similar curves were obtained for the reactions carried out isothermally at the other temperatures, and the rate constant (k^*) for each of these is shown in Table 2. It is likely that these rate constant values are a composite of reaction rate constants for bond cleavage reactions and other constants for diffusion and dissolution of the coal macromolecules in the supercritical phase. Because of the variety of bonds in the coal matrix which must be broken to solubilize the coal, the range of individual rate constants for bond cleavages which make up the composite might be quite large. Similarly, the polydispersity of molecular sizes in the material released by bond breakage and the solvation parameters of these materials might result in diffusion constants that vary over a large range. Thus one would not expect to be able to derive an activation energy for bond dissociation from the rate constant data at the different temperatures via an Arhenius plot.

Comparison of the rate constants for the 350, 380, and 400°C runs show that they increase generally with the temperature as one would normally expect. The rate constant for the 325° reaction is higher than that for the 350° reaction, but this is for much less extracted material, a 10% yield versus a 28% yield. Thus at 325° we observe the rate constant for the easily extracted material (10% yield) and the rate constant for extraction of this material would be expected to increase with temperature. Then at 350°C the less easily extracted material contributes to the extraction products (an additional 20% yield) but with a lower extraction rate constant, hence lowering the overall rate constant observed. At higher temperatures the rate constant for the less easily extracted material increases. At the lower pressures, lower yields are obtained, presumably because of lower solvent density. This may be the same easily extracted material with the higher extraction rate constant, exhibiting the expected increase with temperature. Thus the less easily extracted material made no contribution to the rate constant at the lower pressures.

For the Wyodak coal extracted at 380° and 4.5 MPa, the micropore surface calculated from the scattering data was $2.7 \times 10^3 m^2/g$. This substantial (tenfold) increase was accompanied by a decrease in the transition pore area to 0.39 m^2/g. Progressive isothermal (380°C) extraction as a function of pressure was carried out at 4.5, 7.5, and 10.5 MPa. The curves show an increase in scattering at the intermediate h values, which can be attributed to an increase in the transition pore structure (Table 1). There is also a small increase in the scattering at the larger h values following extraction at 7.5 MPa which suggests additional micropore structure. The progressive changes in the micropore surface area may be due to the increased

solubility of the extract at higher fluid density. The increased transition pore structure is likely a consequence of heterogeneous nature of the coal which results in certain regions dissolving more easily than others.

The change in kinetics as the reaction proceeds may be attributed to an increase in surface area as the micropore volumes develop during the extraction. Thus the greater contact with solvent in the enlarged micropores may result in release of more coal material, even though the activation energies for bond cleavage do not change. Further measurements are needed to confirm this hypothesis.

Experiments were carried out with two additional coals, Beulah (ND) lignite and Pittsburgh #8 bituminous coal (Argonne premium sample), with supercritical THF at 2200 psi and 380°C. The bituminous coal gave a 24% yield of extract in a two-hour run. The uv response had not reached the baseline even after the two hours, indicating that coal-derived material was still being extracted. As expected from this incompleteness of the reaction, the first-order rate constant calculated from the uv response curve for this experiment was considerably lower than that of the Wyodak at the same temperature and pressure, that is 0.014 min^{-1}. Thus the bituminous coal is capable of giving good yields of extract but at a much slower rate than the Wyodak subbituminous coal. Under the same conditions of temperature and pressure, the Beulah lignite gave a yield of 12% over a 80-min period, with the uv response returning to baseline. The uv response curve was unlike that of the Wyodak and Pittsburgh #8 in that the maximum extraction rate was reached more slowly. The first-order rate constant calculated from the curve was 0.022, also lower than that of the Wyodak. These data appear to provide an excellent reactivity index for the coal under nonreductive conditions.

REFERENCES

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2. Kalliat, M.; Kwak, C.Y.; Schmidt, P.W. New Approaches in Coal Chemistry, Symposium Series 169; Amer. Chem. Soc.: Washington, DC, 1981; Chapter 1.

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ACKNOWLEDGEMENTS

Table 1
Scattering Results for Wyodak Coal

Conditions	Specific Surface (m^2/g)			Specific Volumes x 10^3 (cm^3/g)	
	S_{ma}	S_{tr}	S_{mi}	V_{tr}	V_{mi}
120 C, Ar, 0.2MPa	1.5	3.7	58	2.2	7.1
120 C, THF, 4.5MPa	1.8	3.0	2.9×10^2	2.2	26
380 C, THF, 4.5MPa	1.6	0.39	2.7×10^3	0.15	140
380 C, THF, 7.5MPa	1.2	4.5	4.0×10^3	2.3	250
380 C, THF, 10.5MPa	1.5	10.0	4.3×10^3	4.0	260

Table 2
Yield data and apparent rate constants for Wyodak extractions (THF)

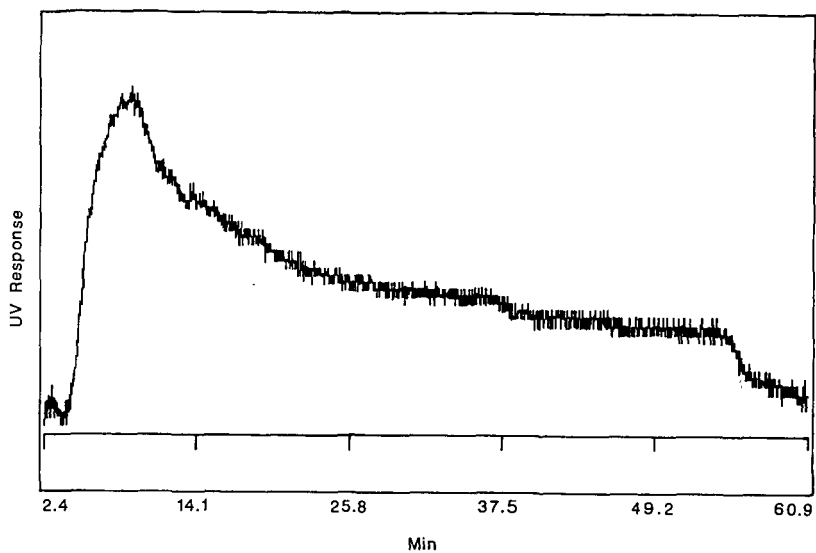| Temperature (^{O}C)	Pressure (MPa)	Yield (%mf±2%)	k^*(min^{-1})
325	15.2	10	0.041
350	15.2	28	0.028
380	15.2	30	0.041
400	15.2	25	0.064
380	10.3	9	0.053
380	5.5	6	0.052

Figure 1: UV response curve for supercritical THF extraction of Wyodak. (THF, 380°, 2200 psi, 1 ml/min).